PATENT SPECIFICATION

(54) POROUS MATERIALS DERIVED FROM TETRAFLUOROETHYLENE AND PROCESS FOR THEIR PRODUCTION

(71) We, W. L. GORE & ASSOCIATES, INC., a Corporation organised and existing under the laws of the State of Delaware, United States of America, of 555 Papermill Road, Newark, Delaware 19711, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to porous materials made of polymers containing units derived from tetrafluoroethylene.

Polymers derived from tetrafluoroethylene, particularly the polymer polytetrafluoroethylene, are becoming increasingly widely used because of their chemical inertness and their desirable physical properties such as water repellancy and electrical insulating properties. However, the production of porous articles from such polymers has presented considerable difficulties. Porous products which have been made are difficult to keep porous and the provision of adequate strength presents problems. Complicated and expensive processes have been devised such as adding a filler to the polymer prior to shaping and then removing the filler after shaping, for example, by leaching it out of the shaped article with a solvent, or by melting or burning it out. Not only are such process steps time consuming but the cost of such processes make them unattractive commercially.

According to the present invention there is provided a porous polymeric material containing units derived from tetrafluoroethylene, the material having a microstructure characterized by nodes interconnected by fibrils, the material having a matrix tensile strength (as herein defined) of at least 7,300 p.s.i.

Further according to the invention there is provided a process for the production of a porous polymeric material containing units derived from tetrafluoroethylene, which process comprises forming a shaped article of the polymer by a paste-forming extrusion technique, and expanding the shaped article after removal of lubricant therefrom, by stretching the shaped article at an elevated temperature and at a rate exceeding 10% per second of its original length.

As used herein, the term "matrix tensile strength" means the product of the maximum tensile strength of the material (generally, the longitudinal tensile strength) and the ratio of the specific gravity of the solid polymer divided by the specific gravity of the expanded, porous product. For polytetrafluoroethylene, the specific gravity of the solid polymer is about 2.3 if the polymer has never been heated to temperatures above its crystalline melt point, and about 2.15 for polymer which has been heated to above its crystalline melt point.

Porous materials in accordance with the invention generally have a good combination of porosity and strength. In this regard they are generally better than previously available fluorocarbon polymers. The porous materials are permeable and they can be laminated, impregnated, and bonded to provide composite structures.

The porous materials in accordance with the invention produced by expansion of a paste-formed article of a polymer derived from tetrafluoroethylene at an elevated temperature and at a rate exceeding 10% per

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second, can subsequently be heat treated to increase their strength further, whilst retaining a porous structure. Paste-forming techniques are used to convert a paste of the polymer into a shaped article which is then expanded, after removal of lubricant used in the shaping, by stretching in one or more directions. After the stretching, the polymer is preferably heated to at least 327°C under tension, after which it is cooled the porosity produced by the expansion is subsequently retained in subsequent steps for there. is usually little or no coalescence or shrinkage upon releasing the cooled product.

Paste-forming methods of forming articles from dispersion polymerized polytetrafluoroethylene are well known commercially and such methods can be used to produce articles for treatment in accordance with the invention. Extrusions of various cross-sectional shapes such as tubes, rods and tapes have been produced from a variety of resins or polymers derived from tetrafluoroethylene. Other paste-forming operations such as calendering and molding are also practiced commercially. The steps in paste-forming include mixing the resin or polymer with a lubricant, such as an odourless mineral spirit, and carrying out forming steps in which the polymer resin is subjected to shear, thus making the shaped articles cohesive. The lubricant is removed from the extruded shape, usually by drying. Hitherto, such unsintered products are heated above the melting point of the polymer, generally about 327°C., causing it to sinter or coalesce into an essentially impermeable structure. The unsintered product is used in processes in accordance with the present invention.

Paste-formed, dried, unsintered shapes produced by such hitherto proposed processes are then expanded by stretching in one or more directions under certain conditions so that they become substantially more porous and stronger. Expansion with an increase in strength occurs with certain preferred tetrafluoroethylene resins within preferred ranges of rate of stretching and preferred ranges of temperature. The preferred temperature range is from 35°C to 327°C. At the lower temperatures within this range it has been found that there is a maximum rate of expansion beyond which fracture occurs, as well as a lower limit beneath which fracture also occurs or where weak materials are obtained. The lower limit is of much more practical significance. At high temperatures within this range, only a lower limit of rate has been detected. The lower limit of expansion rate depends on temperature in a roughly logarithmic fashion, being much higher at higher temperatures. Most, but not all, of the preferred materials in accordance with the invention are obtained when expansion is carried out at the higher temperatures within

the range of 35°C to 327°C. The balance of orientation in the extruded products also affects the relationship between the preferred range of rates of expansion and temperature.

It has been found that some polymers can be more readily expanded than others, since, they can be processed over wider ranges of rates of expansion and temperatures, and still produce useful products. The polymers to be expanded should generally be of high crystallinity, preferably in the range of 98% or above, and correspondingly of low amorphous content. It has been found that techniques for increasing the crystallinity of the polymers, such as annealing at high temperatures just below the melt point of the polymers, generally serve to improve the performance of the polymer in the expansion process. Copolymers of tetrafluoroethylene, which generally have defects in crystal structure that increase the amorphous content, usually do not work as well as homopolymers. However, it has been found, for example, that copolymers containing units derived from less than 0.2 wt% of hexafluoropropylene can be made to work if high rates of expansion are used at temperatures just below the melt point of the polymer.

The precise form of the porous microstructure of the expanded polymers generally depends upon the temperature and the rate at which the polymer is expanded. However, the microstructure of materials in accordance with the invention consists of nodes interconnected by fibrils. In the case of uniaxial expansion the nodes are elongate, the longer axis of a node being substantially perpendicular to the direction of expansion. The fibrils which interconnect the nodes are substantially parallel to the direction of expansion. The fibrils appear to have characteristic maximum and minimum cross-sectional dimensions, the maximum width usually being about 0.1 micron (1000 Ångstroms), which is about the diameter of the crystalline particles, and the minimum width usually being one or two molecular diameters (i.e. in the range of 5 or 10 Ångstroms). The nodes may vary in size, for example, from about 400 microns to less than one micron, depending on the conditions used in the expansion. The term "microstructure" is used herein to refer to such structures which are of a size such that they cannot be resolved with the naked eye. Materials produced by expansion at high temperatures and high rates generally have a more homogeneous structure than those produced at lower temperatures and rates, i.e. they have smaller, more closely spaced nodes and these nodes are interconnected with a greater number of fibrils. Such materials have been found to have much greater strength.

It should be noted that during the expansion large increases in strength are introduced

into the polymer, both porosity and strength increasing, so that a more than ten-fold increase in strength can be obtained. British Patent Specification No. 1,279,364, describes a process for expanding unsintered polytetrafluoroethylene sheets, rods and other shapes to give low density, low strength products. However, by performing the stretching at a rate exceeding 10% per second, a surprising increase in strength can be obtained. Although most materials fracture when subjected to a high rate of strain, highly crystalline polytetrafluoroethylene can withstand this treatment without breaking.

When polymers which have been expanded in accordance with the invention are heated to above the lowest crystalline melting point of the polymer, for example of polytetrafluoroethylene, disorder begins to occur in the geometric arrangement of the polymer crystallites, and the crystallinity decreases with a concomitant increase in the amorphous content of the polymer, typically to 10% or more. These resulting amorphous regions within the crystalline structure appear greatly to inhibit slip along the crystal axes of the crystallites and they appear to lock fibrils and crystallites so that they resist slip under stress. This effect is referred to herein as "amorphous locking". Therefore, the heat treatment may be considered to be an amorphous locking process. One important aspect of amorphous locking is that the amorphous content of the polymer increases, regardless of the crystallinity of the starting polymer. Whatever the explanation, heat treament above 327°C after expansion can provide a surprising increase in strength, often doubling that of the unheat-treated but expanded material.

Because the upper end of the melting range of polytetrafluoroethylene is about 345°C, the heat treatment after expansion appears to be more effective above this temperature, although lower temperatures can be used if the exposure time is long enough. The heat treatment temperature is preferably in the range of 350°C to 370°C, and the heating may, for example, range from 5 seconds to one hour. The microstructure of the expanded product generally remains substantially unchanged as a result of the amorphous locking step. However, if the amorphous locking is carried out at too high a temperature for too long a time, the microstructure may become coarse with the nodes increasing in size and the fibrils rupturing. If this occurs, there is a noticeable deterioration in strength of the material. However optimum times and temperatures for a given polymer being processed can readily be determined. Temperatures above about 390°C may cause disintegration of structure, and loss of strength, in less than one minute. In heat treating films it is essential that they be held so that they cannot

contract during the amorphous locking process. It is surprising that the expanded polymers do not coalesce during the heat treatment to form high density products. Unexpanded films, having a density of about 1.5 gm/cm³ when so heated have been found to coalesce to form essentially void-free materials having a room temperature density of about 2.15 gm/cm³. Very little increase in density usually occurs when expanded polymers having a density of less than 1.00 gm/cm³ are heated above 327°C.

The increase in strength of the polymer matrix is dependent upon the strength of the extruded material before expansion, the degree of crystallinity of the polymer, the rate and temperature at which the expansion is performed, and the amorphous locking. When all these factors are employed to maximise the strength of the material, tensile strengths of 10,000 psi and above, with a porosity of 90% or more, can be obtained. In these cases the polymer matrix can have strengths in excess of 100,000 psi. In contrast, the maximum tensile strength of conventional extruded or molded polytetrafluoroethylene after sintering is generally considered to be about 3,000 psi, and for conventional extruded and calendered polytetrafluoroethylene tape which has been sintered the maximum is about 5,100 psi.

As indicated above, some of the properties of materials in accordance with the invention are substantially different from those of conventional extruded or molded tetrafluoroethylene-derived polymers. As a result of these differences, the expanded, amorphously locked materials can be used where extruded or molded materials cannot be used.

The materials generally have permeabilities to gases, and in some cases to liquids, which are much higher than those of conventional molded or extruded polytetrafluoroethylene. The permeability to nitrogen of conventional polytetrafluoroethylene film has been reported in the Journal of Teflon, [Jan.—Feb. 1970 (du Pont) at page 10] to be about 1×10^{-10} metric units (Teflon is a registered Trade Mark).

In comparison films of a material in accordance with the invention have been found to have permeabilities to nitrogen of generally from 1×10^{-8} to 1×10^{-1} metric units. These higher permeabilities are consistent with the lower densities and high porosities of the expanded, amorphous-locked films, compared with hitherto proposed films. Furthermore, by controlling the degree of expansion and the conditions used for amorphous-locking it is possible to produce tetrafluoroethylene-derived polymeric materials having permeability within the range listed above. Permeability differences are due primarily to differences in pore sizes within the materials.

Permeabilities to liquids are also generally

higher than those of hitherto proposed tetra-fluoroethylene-derived porous materials.

As a result of the ability of materials in accordance with the invention to transmit fluids they can be used as filter membranes to sep-arate solid materials from gases and from liquids. For optimum filtration rates, relatively low-permeability, small pore-size membranes are preferably used to filter out small solid particles, with high-permeability, large pore-size membranes being used to filter out large solid particles.

Also, expanded, amorphous-locked mat-erials in accordance with the invention can be used as semi-permeable membranes for sep-arating wetting fluids from non-wetting fluids. For example, a gas-saturated membrane in contact with water and a gas will transmit the gas, the wetting phase, as described above. It will not transmit the water, the non-wetting phase, as long as the pressure in the water phase does not exceed the water entry pres-sure for that particular combination of mem-brane and fluids.

One factor which influences entry pressure of a non-wetting fluid into a porous material is the size of the pores. Since the size of the pores of expanded, amorphous-locked materials produced in accordance with the in-vention can be and is controlled by the conditions used in the expanding and the amorphous-locking operations, these materials can be used as semi-permeable membranes under a wide variety of conditions. The use-fulness of materials in accordance with the invention as filter membranes for separating solids from fluids, or as semi-permeable mem-branes for separating immiscible fluids from each other, can be enhanced by the fol-lowing, well-known, and highly desirable pro-perties of polymers of tetrafluoroethylene namely:—

(1) outstanding chemical inertness, and
(2) resistance to undesirable physical changes over a wide temperature range.

Expanded, amorphous-locked materials in accordance with the invention can generally be bonded to other materials, or to themselves, more readily than can conventional polytetra-fluoroethylene materials. This is believed to be because bonding agents are able to pene-trate a significant distance into the pores of the expanded, amorphous-locked materials where they remain locked in place after hard-ening. In contrast, there is negligible pene-tration of bonding agents into conventional tetrafluoroethylene polymers, and this, coupled with the general non-bonding nature of low energy surfaces, makes bonding of the conventional materials difficult.

Certain other properties of materials in accordance with the invention are better than the corresponding properties of conventional extruded or molded polytetrafluoroethylene products, the former materials thereby being

more useful in many applications than the latter. The thermal conductivity of molded conventional polytetrafluoroethylene is about 1.7 Btu/hr/sq.ft/°F./in. whilst that of the expanded, amorphous-locked polymer in ac-cordance with the present invention gener-ally ranges from one-tenth to one-half that value. In line with this, the more highly expanded materials in accordance with the invention have proven to be useful thermal insulators.

Similarly, expanded, amorphous-locked polytetrafluoroethylene in accordance with the invention has shown an advantage over the conventional homopolymer in the previously proposed forms, as an electrical insulator in coaxial cables. The lower dielectric constant of the former, generally about 1.2 to 1.8, compared with 2.2 for the conventional poly-mer, permits smaller and lighter cables to be constructed using materials in accordance with the invention. Many applications in which weight-saving (i.e. the use of low den-sity materials) is an advantage can benefit by using the expanded, amorphous-locked polymers in preference to conventional high density tetrafluoroethylene polymers.

The invention will be further understood by reference to the examples given below and to the accompanying diagrammatic draw-ings, all of which are given for illustrative purposes only. In the drawings:

Figure 1 is a plan view of a section of an expanded amorphously locked tetrafluoro-ethylene polymer as seen under a microscope; and

Figure 2 is a view of apparatus for use in producing materials in accordance with the invention.

As shown in Fig. 1, the expanded, amor-phously locked, porous material 10 comprises a plurality of nodes 11 orientated perpendic-ular to the direction in which expansion was effected. These nodes, on the average about 50 microns in size, are fairly irregular in shape, and they lie closely together and in many instances appear to touch at points. A given node is connected to adjacent or nearby nodes by fibrils 12 which generally vary in length from 5 to 500 microns depend-ing upon the amount of expansion. While Fig. 1 shows the effect of uniaxial expansion, it will be appreciated that with biaxial expan-sion and expansion in all direc-tions, similar fibril formation occurs in said directions with the production of spider's-web-like or crosslinked configur-ations and an attendant increases in strength. The porosity also increases as the voids or spaces between the polymeric nodes and fibrils become more numerous and larger in size.

The apparatus shown in Fig. 2 is herein-after described in Example 5.

In the Examples, materials produced in

accordance with the invention had a micro-structure characterized by nodes interconnected by fibrils.

EXAMPLE 1.

Expansion of Rods.

A cylindrical rod of 5/32 inch diameter was made by extruding a paste of "Teflon" 6A polytetrafluoroethylene, in 130 cc/lb. of mineral spirits as an extrusion aid, at a reduction ratio of 370 (the resin being obtainable from E. I. du Pont de Nemours & Co., Inc.). The volatile extrusion aid was removed by drying, the resultant rod having a specific gravity of 1.63, a tensile strength of 531 psi, and an elongation of 183% (A.S.T.M. test method). The amorphous content of the "Teflon" 6A resin and the unsintered rod were determined using the infra-red method described by R. E. Moynihan, in "IR Studies on Polytetrafluoroethylene", J. Am. Chem. Soc. *81*, 1045—1050 (1959), and found to be 1.5%.

An apparatus was devised so that samples of the rod could be stretched by various amounts at controlled rates and controlled temperatures. The apparatus consisted of two clamps for holding the rod, one clamp being held fixed within an oven while the other clamp was attached to a wire leading outside the oven to a rack-and-pinion pulling device driven by a variable speed motor. After the sample had been expanded by stretching at the given controlled temperature, the oven temperature was raised to 370°C for ten minutes while the samples were held clamped in their extended condition. The samples were thereafter cooled to ambient temperature. In some cases the samples broke during the expansion step and this is noted in the tables below. The term "broke" refers to the fact that the particular sample being tested broke under the conditions given as an attempt was being made to stretch it to the final elongation given; the precise percentage of elongation at which the given sample broke is not given.

As can be seen in Table 1A, all samples were successfully expanded to a porosity of about 68% under the conditions of temperature and rate of stretch shown. Table 1B shows that samples at the lower values of temperature rate could not be expanded by stretching 550%, while the rest of the samples were successfully expanded to a porosity of about 84%. Table 1C shows that only two samples were successfully expanded when the stretch was 1500%. These samples were obtained at the highest values of rate and temperature and had a porosity of about 96%.

TABLES 1A, 1B and 1C

TABLE 1A: Percent Stretch=200

Temperature °C	Rate of Stretch 30%/Sec.	Rate of Stretch 100%/Sec.	Rate of Stretch 1000%/Sec.	Rate of Stretch 5000%/Sec.
93	67% porosity	67% porosity	67% porosity	66% porosity
204	66% ,,	68% ,,	67% ,,	66% ,,
315	66% ,,	66% ,,	67% ,,	68% ,,

TABLE 1B: Percent Stretch=550

93	broke	broke	broke	broke
204	broke	84% porosity	85% porosity	85% porosity
315	broke	84% ,,	84% ,,	83% ,,

TABLE 1C: Percent Stretch=1500

93	broke	broke	broke	broke
204	broke	broke	broke	broke
315	broke	broke	96% porosity	96% porosity

This example illustrates that highly expanded products in accordance with this invention can be obtained when the expansion is carried out at high temperatures and high rates of stretch. The amorphous content of these porous rods was found to be 24%.

EXAMPLE 2.
Expansion of Rods.

Rods 5/32 inch in diameter were manufac-

tured under conditions similar to Example 1, except that "Teflon" 6C polytetrafluoroethylene was used, this also being obtainable from the du Pont company. The amorphous content of the "Teflon" 6C, and the unsintered rod, were found to be 3.5%. While effective expansion was not obtained under the conditions of Example 1, at very much higher expansion rates, the desired expansion did occur:

TABLE 2: Percent Stretch=550

Temperature °C	Rate of Stretch 5,000%/sec.	Rate of Stretch 10,000%/sec.	Rate of Stretch 40,000%/sec.
93	broke	broke	broke
204	broke	broke	68% porosity
315	broke	broke	68% porosity

Amorphously locking the porous products obtained using the 40,000%/sec. rate of expansion was then effected, and the microstructure of the products conformed to such as is shown in Fig. 1. The amorphous content after heat treatment at 370°C followed by cooling was 35%.

EXAMPLE 3.
Expansion of Films.

The following experiments were performed using a pantograph, which is a machine capable of stretching films biaxially or uniaxially over a range of rates and temperatures. The pantograph used in these experiments was capable of stretching 4" × 4" samples of film to 16" × 16". The 4" × 4" film was gripped on each side by 13 actuated clamps, which moved apart uniformly on a scissor mechanism. The film was heated by hot air flow from above and below.

A sample of film 6 inches wide, 0.036 inch thick, and of continuous length was produced by the paste extrusion process from "Teflon" 6A polytetrafluoroethylene using 105 cc of mineral spirits per pound of resin as an extrusion aid. After removing the extrusion aid by drying, the unsintered film was found to have the following properties: specific gravity of 1.65, longitudinal tensile strength of 300 p.s.i. and transverse tensile strength of 250 p.s.i.

Ex. 3(a) A 4" × 4" sample of this film was conditioned for approximately 4 minutes at

225°C in the pantograph and then stretched biaxially at a rate of 500%/sec in each direction to a size of 16" × 16". The temperature of the film was then raised to 370°C for 5 minutes while held clamped in the extended condition. The film was then cooled to ambient temperature and the following properties were found: specific gravity of 0.15, longitudinal tensile strength of 2,500 p.s.i. (a matrix tensile strength of 36,700 p.s.i.) and transverse tensile strength of 2,230 p.s.i.

Ex. 3(b): A sample was prepared in all ways similar to Example 3(a) except that it was stretched in the pantograph at the lower rate of 55%/sec. The resulting film was still cohesive but was found to have weak areas, and a non-uniform appearance.

Ex. 3(c): A sample was prepared in all ways similar to Example 3(a) except that it was stretched at the even lower rate of 5%/sec. The film did not expand, but ruptured.

Ex. 3(d): A sample was prepared in all ways similar to Example 3(a) except that the temperature during expansion was 50°C. This film did not expand, but ruptured.

Ex. 3(e): A sample of paste-extruded film was taken before removal of the extrusion aid and calendered to a thickness of 0.0043 inch. The physical properties of the film were measured: specific gravity of 1.60; longitudinal tensile strength of 2,200 p.s.i., and transverse tensile strength of 270 p.s.i.

Samples of this film were stretched on the pantograph. The results are summarized in Table 3.

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TABLE 3

Example 3(e)

Temperature °C	Expansion Rate In Longitudinal Direction (%/sec.)	Expansion Rate In Transverse Direction (%/sec.)	Result
225	500	500	Ruptured
225	500	0	Long. Tensile=3900 psi (a matrix tensile strength of 12,800 p.s.i.) Trans. Tensile=1150 psi Spec. Gravity=0.70
225	0	500	Ruptured
50	500	500	Ruptured
50	500	0	Ruptured
50	0	500	Long. Tensile=2400 psi (a matrix tensile strength of 7,360 p.s.i.) Trans. Tensile=2700 psi Spec. Gravity=0.75
225	5	5	Ruptured
225	5	0	,,
225	0	5	,,
50	5	5	,,
50	5	0	,,
50	0	5	,,

From the tabulated results, it can be seen that the film responded differently depending on which axis was stretched but that at the
5 low rates rupture occurred irrespective of the direction of expansion.

EXAMPLE 3(f)
Expanded Films Made by Biaxial Stretching.
Another 4" × 4" sample of film of the type
10 described in the second paragraph of Example 3 above was stretched in the pantograph machine. In this case, the film was stretched simultaneously in two directions at right angles to each other, 100% in each direction. Thus,
15 the surface area of the stretched film was four times the surface area of the original film.

The film temperature was about 300°C.

during the stretching operation. Linear stretching rates of about 400% per second 20 in each dimension were used.

With the expanded film still in tension (stretcher clamps still holding the stretched film), hot air was circulated over the film such that the film temperature was about 25 360°C. for five minutes. This caused amorphous locking within the film.

Finally, with the stretcher clamps still holding the film, the film was cooled rapidly to room temperature by blowing cold air 30 against it. The cooled film, which was then removed from the clamps, was the desired expanded, amorphous locked film.

Properties of the original unexpanded film and of the final expanded, amorphous-locked 35 film, are listed below.

TABLE 4

Property	Original Unexpanded Film	Expanded, Amorphous-Locked Film
Film Length, relative units	1	1.9
Film Width, relative units	1	2.0
Film Thickness, mils	36.0	31.5
Specific Gravity	1.65	0.45
Long. Tensile Strength, psi	300	1900 (a matrix tensile strength of 9,290 psi)
Transverse Tensile Strength psi	250	1760
Permeability to air, metric units	4×10^{-5}	6×10^{-3}

EXAMPLE 4.
Expansion of Filled Films.

The "Teflon" 6A polytetrafluoroethylene identified above, was blended with a commercially available asbestos powder in a proportion of four parts by weight resin to one part asbestos. The mixture was lubricated with 115 cc of odorless mineral spirits per pound of mixture and extruded into a film 6" wide. 0.036" thick, and of continuous length. The film was then calendered to 0.008" thickness and the extrusion aid removed by drying. The properties were measured and found to be as follows: specific gravity of 1.44, longitudinal tensile strength of 1,000 psi; and transverse tensile strength of 205 psi.

A 4" × 4" sample was mounted in the pantograph described above and stretched at a rate of 500%/sec. at a temperature of 225°C. and to three times its original length in the longitudinal direction while no stretch was applied in the transverse direction. A sample of the film was tested and found to have the following properties: specific gravity of 0.82, longitudinal tensile strength of 1500 psi, and transverse tensile strength of 145 psi. The remainder of the sample was placed in clamps to restrain it from shrinking. It was heated to 370°C for five minutes, and then cooled to ambient temperature. The following properties were measured on this sample: specific gravity of 0.95, longitudinal tensile strength of 2,900 psi, and transverse tensile strength of 750 psi.

The heat treating of the film substantially increased its tensile strength as can be seen from the above values, and it had a very little effect on specific gravity.

EXAMPLE 5.
Manufacture of Continuous Lengths of Porous Film.

A machine was constructed for manufacturing long lengths of expanded film. Referring to Fig. 2, an unsintered polytetrafluoroethylene film 13 from a paste extrusion processes fed to the machine from roll 14 onto heated roll 15 where the film is preheated to the temperature at which it is to be expanded. Rolls 15 and 16 are of the same diameter and are connected through a gear box so that their relative rates of rotation can be changed. Roll 16 can be driven faster than roll 15 so that the film can be stretched in the gap "A" between the rolls thereby making the film expand. The difference in speed between rolls 15 and 16 determines the amount of stretch and thus the amount of expansion. For example, when roll 16 is driven twice as fast as roll 15, the film is expanded approximately 100% because, unlike other films, the unsintered polytetrafluoroethylene film changes very little in thickness or width but its length increases by 100%. The increase in volume of the polymer is due to an increase of porosity, and a corresponding decrease of specific gravity. The relative positions of rolls 15 and 16 are adjustable so that the gap "A" between them can be varied. This allows one to control the rate of expansion. For example, when the gap distance is halved, the rate of expansion is doubled. It should be noted that the rate of expansion is also affected by the rate at which the film is fed into the machine. Roll 16 is maintained at the same temperature as roll 15. Expanded film leaves roll 16 and goes onto a hot roll 17 (running at the same peripheral speed as

roll 16) where the film is heated to approximately 370°C so that amorphous locking occurs. The residence time of film on this roll is controlled by the position of roll 18, which can be moved around the periphery of roll 17. Roll 19 is water-cooled to reduce the temperature of the film as it passes thereover and before being wound up on roll 20.

Thus, with this machine one is able to control three important variables in expanding the tetrafluoroethylene polymer film, i.e. the temperature, the rate of expansion, and the amount of expansion.

Data for three runs on this apparatus is given in Table 5.

TABLE 5

Resin:	(a) "Fluon" CD-1 (obtainable from Imperial Chemical Industries Ltd; Fluon is a registered Trade Mark)	(b) "Teflon" 6A	(c) "Teflon" 6A preheated 3 hrs. at 3000°C. prior to paste extrusion
Properties of starting Film:			
Thickness of Film	0.0050"	0.0050"	0.0050"
Density, gm/cm^3	1.47	1.52	1.54
Longitudinal tensile, psi	1600	1900	2650
Transverse tensile, psi	200	250	350
Processing Conditions:			
Tape feed rates: roll 14 to roll 15	30 ft./min.	30 ft./min.	30 ft./min.
Temp., rolls 15 and 16	300°C.	300°C.	300°C.
Roll speed ratio: roll 15: roll 16	1:2.87	1:2.87	1:2.87
Calculated Rate based on 3" stretch length	574%/sec.	574%/sec.	574%/sec.
Temp. for roll 17	370°C.	370°C.	370°C.
Dwell time on roll 17	3 sec.	3 sec.	3 sec.
Properties of Final Film:			
Thickness	0.0047"	0.0048"	0.0046"
Density, gm/cm^3	0.66	0.67	0.73
Long. Tensile, psi	2850 (matrix tensile strength of 9,500 psi)	4000 (matrix tensile strength of 13,000 psi)	8950 (matrix tensile strength of 27,000 psi)
Transverse tensile, psi	850	1050	1300

EXAMPLE 6.
Expanded Films Made by Vacuum Forming.

The starting material was an extruded, unsintered "Teflon" 6A polytetrafluoroethylene film with a specific gravity of 1.50 and a thickness of 3.9 mils produced by a paste-forming technique. A rectangular section of this film was placed in a vacuumforming device, the temperature of which could be raised with an electric heater or lowered with a stream of cold air. The film was clamped in place, and the temperature of the assembly was raised to about 300°C. Then the pressure in the expansion chamber was reduced rapidly, causing the film to be stretched very rapidly to about three times its original area into the shape of a bowl.

Without releasing the vacuum, the tem-

perature of the assembly was raised to about 350°C where it was held for about ten minutes. The assembly was then cooled as rapidly as possible by blowing cold air, and finally the vacuum was released and the ex-

panded, amorphous-locked film was removed from the vacuum-forming device.

Properties of the original film and the expanded, amorphous-locked film are listed below.

TABLE 6

Property	Original Unexpanded Film	Expanded, Amorphous-Locked Film
Film area, relative units	1.0	2.1
Film Thickness, mils	3.9	3.7
Specific Gravity	1.50	0.75
Long. Tensile strength, psi	1800	4100
Transverse tensile strength, psi	240	1400

The greatly enhanced strengths and porosities that can be achieved by this invention are clearly shown in the above table.

EXAMPLE 7.
Expanded, Amorphous-Locked Film Made By Stretching Using a Molding Device.

A section of extruded, unsintered polytetrafluoroethylene film produced by a paste-forming technique was fastened to a female member of a molding device, and the assembly was heated to 275°C by circulating hot air over it. Then a bowl-shaped male member was rapidly forced against the film causing it to stretch to about three times its original surface area, without crushing the stretched film between the members of the molding device.

With the film still held in place, the entire assembly was heated to about 340°C for 15 minutes, after which it was cooled to ambient temperature. Then the clamps holding the film were released to give the desired expanded, amorphous-locked film.

Properties of the original film and the final expanded amorphous-locked film are listed below:

TABLE 7

Property	Original Extruded, Unsintered Film	Expanded Sintered Film
Surface area, relative units	1.0	2.6
Thickness, mils	15	12
Specific Gravity	1.50	0.72
Thermal conductivity Btu/hr/sq.ft/°F./in.	1.5	0.5
Permeability to kerosene metric units	1.9×10^{-7}	28×10^{-7}

EXAMPLE 8.
Expanded Tube Made By Blowing

The starting material was extruded, unsintered "Teflon" 6A polytetrafluoroethylene tubing, produced using a paste-forming technique, having an outside diameter of 0.20 inches and a wall thickness of 30 mils.

A 15 inch long section of this tubing was plugged at one end, and the other end was clamped to a steel tube, which, in turn, was connected to a source of compressed gas.

The tubing was placed in an air oven, and heated to about 300°C. Compressed gas was admitted to the tubing in such a way that the diameter of the tube was increased in about two seconds from the original 0.20 inches to about 0.60 inches. Then, with pressure maintained in the tubing so that no collapse took place, the temperature of the assembly was raised to about 360°C and held there for about five minutes. While still maintaining pressure to prevent tubing collapse, the as-

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sembly was cooled rapidly using a stream of cold air, yielding the desired expanded, amorphous-locked tubing.

Properties of the original tubing and the expanded, amorphous-locked tubing are as follows:

TABLE 8

Property	Original Unexpanded Tubing	Expanded, Amorphous-Locked Tubing
Length, relative units	1.0	0.8
Outside diameter, inches	0.20	0.56
Wall thickness, mils	30	24
Specific gravity of tubing walls	1.50	0.75
Air permeability of tubing walls, metric units	2×10^{-5}	1×10^{-3}

Due to its high permeability, the above expanded, amorphous-locked tubing was useful as a filter membrane for separating solids from fluids.

EXAMPLE 9.
Expanded, Amorphous-Locked, Laminated Film made from two layers of Expanded Film.

Using a tape expanding machine as illustrated in Fig. 2 with the roll 17 at 300°C (a temperature below the amorphous-locking temperature) a sample of expanded, "Teflon" 6A polytetrafluoroethylene film was made. The initial film was produced by a paste-forming technique. The expanded film had a specific gravity of 0.60, a longitudinal tensile strength of 1900 psi (a matrix tensile strength of 7,300 psi), a transverse tensile strength of 110 psi, and a thickness of 3.5 mils.

Two samples of this film were placed at right angles to each other, one on top of the other and clamped to a rigid frame which was secured by all four edges of the resulting sandwich. One film was thereby lightly pushed against the other over the whole area of contact. This assembly was then amorphously locked by heating to about 370°C for 7 minutes. Then the assembly was rapidly cooled with a stream of cold air, and the clamps were released to yield the desired one-piece laminated film.

The tensile strength of the expanded, amorphous-locked laminate was 4300 psi in each direction. Its thickness was 6.4 mils.

EXAMPLE 10.
An expanded, Amorphous-Locked Film as a Filter Membrane Or as a Semi-Permeable Membrane.

An extruded, calendered, unsintered "Teflon" 6A polytetrafluoroethylene film was made using a conventional paste-forming procedure described above. The film was expanded and amorphously locked using a machine as shown in Fig. 2 and a process in accordance with the invention. Expansion was carried out at a temperature of about 300°C, and amorphous locking at about 370°C. Properties of the original film and the expanded, amorphous-locked film are listed below:

TABLE 9

Property	Original Unexpanded Unsintered Film	Expanded Sintered Film
Thickness, mils	4.0	3.5
Surface area (length × width), relative units	1.0	2.8
Specific Gravity	1.46	0.60
Permeability to air, metric units	1.0×10^{-4}	0.032
Permeability to kerosene, metric units	7.0×10^{-7}	2.3×10^{-4}

Smoke-containing air was filtered through a sample of the expanded, amorphous-locked film. The filtered air was clean, and the filtration rate was relatively high. A similar attempt to filter smoke-containing air using a sample of the unexpanded, unsintered film described above was unsuccessful because the filtration rate was too low.

Samples of the expanded, amorphous-locked film were also used to filter solids from suspension of solids in various organic liquids. Again, good separations were obtained, and filtration rates were reasonably high. However similar attempts using samples of the unexpanded, unsintered film were unsuccessful because of the extremely low filtration rates.

When an effort was made to flow water through the expanded, amorphous-locked film when containing air using a 5 psi flow pressure, no flow occurred. However, when the flow pressure exceeded 10 psi flow started, and thereafter the flow of water through the membrane was quite similar to that of organic liquids which wet the membrane. This membrane was found to be useful in separating solids from dispersions of the solids in water.

A sample of the expanded, amorphous-locked film was fitted into the cone of a conical filter funnel, and a mixture of kerosene and water was poured into the funnel. The kerosene flowed through the film at a reasonably rapid rate, but no water penetrated the film since the pressure of the water phase was lower than the water entry pressure into either the gas-saturated or the kerosene-saturated film. Thus, the expanded, amorphously locked film was found to be an effective semi-permeable membrane in sep-

arating fluids that wet tetrafluoroethylene polymers from non-wetting fluids. Similar attempts to use the corresponding unexpanded, unsintered film as a semi-permeable membrane were unsuccessful because of the extremely low flow rates involved.

EXAMPLE 11.
Expanded, Amorphously Locked Film Impregnated with Poly(Methyl Methacrylate).

A part of an expanded, amorphous-locked film produced as described in Example 10 was painted with a freshly made solution of 1% of a polymerization initiator in methyl methacrylate. The solution was rapidly absorbed into the expanded, amorphously locked film. Any excess solution not so absorbed was wiped from the surface of the film.

Then the impregnated film was warmed, causing the methyl methacrylate to polymerize within the pores of the expanded, amorphous-locked film, to yield a film having pores filled with poly(methyl methacrylate).

The comparison shown below of the properties of conventional extruded, calendered, unsintered polytetrafluoroethylene film with those of the expanded, amorphous-locked, film impregnated with poly(methyl methacrylate) shows clearly that the impregnated film has the greater dimensional stability without a significant increase in the coefficient of friction. These properties can enable the impregnated materials to be used as bearing materials. The impregnated materials are generally substantially lower in cost than conventional homopolymers or copolymers derived from tetrafluoroethylene.

TABLE 10A

Property	Conventional Unexpanded, Unsintered Film	Expanded, Amorphous-Locked, Impregnated Film
Deformation, 150 psi compressive stress at 25 °C., %	2.7	0.7
Coefficient of Friction against Glass	0.20	0.21

In further impregnation experiments, a piece of expanded, amorphous-locked polytetrafluoroethylene film produced as described in Example 10 was impregnated with the low viscosity epoxy resin, ERLA 2256 (a product of and obtainable from Union Carbide Corporation). A second piece of the film was impregnated with a solution of meta-phenylenediamine in methyl ethyl ketone. When the ketone had evaporated, the two pieces, the longitudinal dimension of one coinciding with the transverse dimension of the other, were placed in contact with each other, and the assembly was heated at about 149°C for about three hours.

The two pieces were firmly bonded by the hardened epoxy resin. Properties of the laminate were as follows:

TABLE 10B

Property	Expanded, Amorphous-Locked Film	Laminate
Longitudinal tensile strength, psi	8,100	8,800
Transverse tensile strength, psi	1,500	8,800
Deformation, 100 psi compressive stress at 25 °C., %	13	1.2
Coefficient of Friction Against Glass	0.14	0.14

EXAMPLE 12.
Use of Expanded, Amorphous-Locked Tape as a core of a coaxial cable.

Expanded, amorphous-locked tape was produced following the procedure described in Example 10. Two such tapes were made, both having a specific gravity of about 0.66, one having a thickness of 2.5 mils, the other, 10 mils. Alternate wraps of (1) the thinner tape, (2) the thicker tape, and (3) the thinner tape, were used to make up a core separating the inner conductor of the coaxial cable from an outer metallic braided shield. A conventional outer jacket of polytetrafluoroethylene covered the shield. The characteristic impedance of the cable was 100 ohms.

A second coaxial cable having an impedance of 100 ohms was produced using a conventional, unexpanded tape to construct the core. After sintering, the density of the polytetrafluoroethylene core was about 2.15 gms/cc.

Because of the lower dielectric constant of the expanded, amorphous-locked polytetrafluoroethylene compared with the conventional polymer, a smaller, lighter cable could be obtained when the expanded, amorphouslocked tape was used. This is shown from the following table.

TABLE 11

Item	A 100 Ohm Impedance Cable made using a core of Conventional Polymer	B 100 Ohm Impedance Cable made using a core of Expanded, Amorphously locked polymer
Conductor Weight g/ft	0.064	0.064
Polymer Insulation g/ft	3.890	0.464
Braided Metal Shield, g/ft	2.700	1.898
Polymer Jacket, g/ft	0.855	0.569
Core Diameter, in.	0.110	0.065
Outer Diameter of Cable, Inch	0.140	0.095
Total Cable Weight g/ft	7.509	2.995

The data listed above show that the use of expanded, amorphous-locked polymer in B rather than the conventional polymer in A as the core of the cable led to a 60% reduction in weight and a 32% reduction in size of the cable.

EXAMPLE 13.
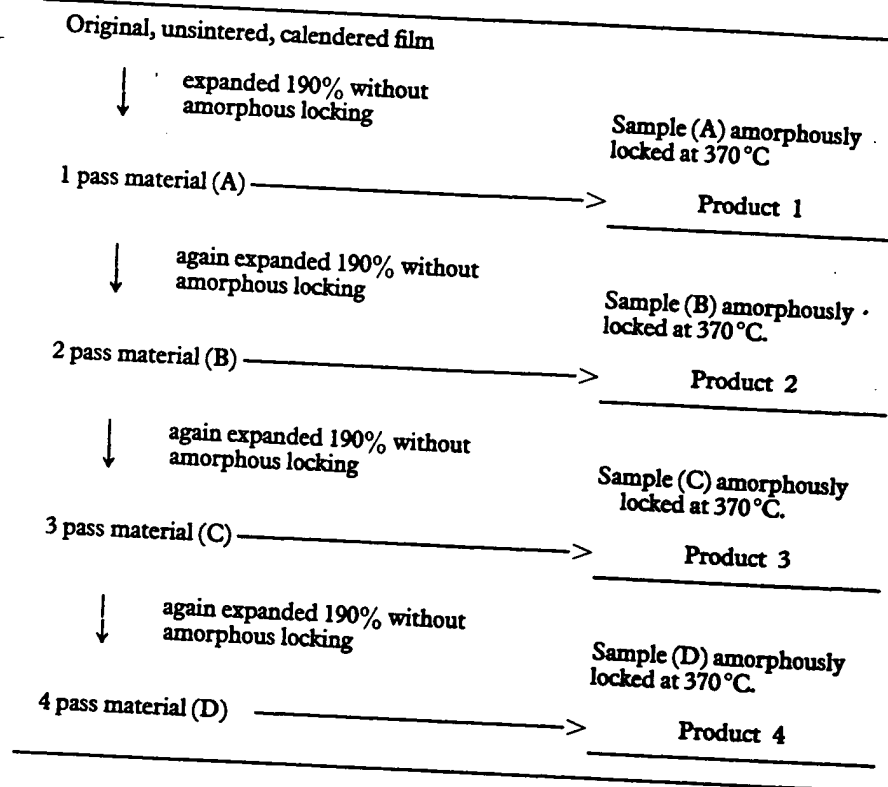*Films which are very greatly Expanded and then Amorphous-Locked.*

Unsintered, extruded, calendered polytetrafluoroethylene film was produced by a pasteforming technique, as described in one of the

earlier Examples. This film had a thickness of 4.0 mils.

Using apparatus as shown in Fig. 2, and the above-described procedures, parts of this film were expanded without amorphous-locking using a stepwise procedure. The machine was set at 190% expansion for each expansion run. Then samples of the expanded films were passed through the machine to lock them amorphously at 370°C without further expansion. The steps followed in this work are explained in the following diagram:

Original, unsintered, calendered film

↓   expanded 190% without amorphous locking

           Sample (A) amorphously locked at 370°C

1 pass material (A) ——————————————————>   Product 1

↓   again expanded 190% without amorphous locking

           Sample (B) amorphously locked at 370°C.

2 pass material (B) ——————————————————>   Product 2

↓   again expanded 190% without amorphous locking

           Sample (C) amorphously locked at 370°C.

3 pass material (C) ——————————————————>   Product 3

↓   again expanded 190% without amorphous locking

           Sample (D) amorphously locked at 370°C.

4 pass material (D) ——————————————————>   Product 4

Properties of the film produced as described above are listed below:

TABLE 12

Film Identity	Expansion %	Thickness mils,	Specific Gravity	Porosity, %	Bulk Long. Tensile Strength, psi	Long. tensile Strength of polymeric matrix, psi
Original film	none	4.0	1.50	35	1,640	2,600
Product 1	190	3.8	0.50	78	2,900	14,000
Product 2	190×2	3.8	0.27	88	2,420	30,000
Product 3	190×2	3.1	0.18	92	2,400	30,000
Product 4	190×4	2.8	0.17	93	2,400	34,000

EXAMPLE 14.

"Teflon" 6A polytetrafluoroethylene was heated for 3 hours at 300°C., cooled, blended with 80 cc of refined kerosene per pound of polymer, and extruded into a film 6 inches wide, and 0.030 inch thick, using a reduction ratio of about 100 (reduction ratio=cross-section area of extrusion cylinder divided by the cross-section of the extrudate). The extruded film was then passed through successive

sets of rolls, each heated to about 80°C., and reduced in thickness from 0.030 inch to 0.002 inch. This film was dried to remove the kerosene and passed through apparatus as shown in Fig. 2 at a rate of 100 ft/min. over roll 15, with rolls 15 and 16 and heated to 320°C and adjusted with their outer peripheries as close together as possible without crushing the 0.002 inch film between them. Roll 16 (and 17, 18, 19) was rotated at a peripheral speed seven times greater than roll 15, thus stretching the film about sevenfold. The film was passed over roll 17 at 370°C and wound up on take-up 20. Rolls 15, 16, 17, 18 and 19 were then adjusted to the same peripheral speed of 30 ft./min., rolls 15, 16 and 17 adjusted to 370°C, and the stretched film passed through the apparatus under these conditions in order to accomplish an adequate heat treatment. The properties of the film after cooling to ambient temperature were as follows:

Thickness	0.0019 inch
Density gm/cm³	0.23

Longitudinal tensile strength 12,200 psi
Longitudinal tensile strength
of polymer matrix 2.2gm/cc × 12,200

$$\frac{2.2\,gm/cc \times 12,200}{0.23\,gm/cc} = 117,000\ psi$$

EXAMPLE 15.
Amorphous Content of Polymer.

A sample of film was prepared as in Example 14 except that it was rolled to a thickness of 0.004 inch. This film was then expanded using the same process as in Example 5 except that roll 17 was not heated. Heat treatments were carried out on samples of this film at 335°C, 350°C, and 390°C for various lengths of time before cooling to ambient temperature. The amorphous content of the polymer was determined at each stage in the process using the infra-red method described by R. E. Moynihan, "IR Studies on Polytetrafluoroethylene", J. Am. Chem. Soc. 81, 1045—1050 (1959). The properties of the films were as follows:

TABLE 13

	Longitudinal Tensile Strength/ Matrix Tensile Strength	% Amorphous	Density (gm/cm³)
"Teflon" 6A powder, heat treated	—	1.5%	
Extruded, dried .004" film	2,650	1.5%	1.5
Expanded not heat-treated	4,200/14,200	1.5%	0.68
Heated to 335°C:			
1 second	5,580/18,500	2.5%	0.60
10 seconds	5,630/18,400	3%	0.70
50 seconds	6,020/19,700	4%	0.70
480 seconds	7,540/24,600	5%	0.70
Heated to 350°C:			
1 second	7,630/24,700	10%	0.70
3 seconds	7,670/24,900	10%	0.70
10 seconds	7,820/25,200	15%	0.70
20 seconds	7,830/24,900	25%	0.70
50 seconds	8,360/26,400	30%	0.70
100 seconds	8,610/27,100	33%	0.70
480 seconds	8,900/27,900	35%	0.70
Heated to 390°C:			
1 second	7,500/23,500	25%	0.71
3 seconds	7,960/23,800	35%	0.73
10 seconds	7,830/23,400	38%	0.73
20 seconds	7,270/20,300	40%	0.78
50 seconds	6,560/16,800	40%	0.85
90 seconds	disintegrated		—

EXAMPLE 16.
High Strength, Low Porosity Films.

A sample of expanded but not heat-treated film from Example 15 was placed in a platen press, compressed at 300 psi and whilst held compressed, the platens were heated to 350°C and then cooled rapidly. The longitudinal tensile strength of the resulting film was 24,000 psi and the density 2.10 gms/cm³, with about 3% porosity. Therefore, it is possible to produce high strength, high density products by compressing the expanded material during the amorphous-locking step. The fibril-node structure is preserved even though the porosity is reduced to about 3%. With higher pressures it is possible to reduce the porosity further and still preserve the high strength of the material.

A second sample of the expanded film from Example 15 which had been heat treated at 350°C for 8 minutes was placed in the press at room temperature and compressed at 1500 psi for several minutes. The film was clear and transparent. Its density was 2.05 gms/cm³ and longitudinal tensile strength was 21,000 psi. Therefore, it is feasible to compress the porous structure of the product and still preserve the high strength of the bulk polymer.

The foregoing Examples show the desirable effect of expansion and amorphous-locking on the tensile strength and density characteristics of the products, and also that high tensile strengths can be retained when the porous structure is compressed.

Porous materials can be produced in accordance with the invention using polytetrafluoroethylene or copolymers of tetrafluoroethylene with other monomers. Such other monomers include, for example, ethylene, chlorotrifluoroethylene, or fluorinated propylenes, such as hexafluoropropylene. Units derived from these monomers should generally be present in only small amounts since it is preferred to use the homopolymer due to its optimum crystalline/amorphous structure with regard to the materials and the process for producing materials in accordance with the invention. Thus, amounts of comonomers should usually be less than 0.2wt% and it is particularly preferred to use polytetrafluoroethylene. While the above Examples show the use of asbestos as a filler, it is to be appreciated that a wide variety of fillers can be incorporated such as carbon black, pigments of various kinds as well as inorganic materials such as, for example, mica, silica, titanium dioxide, glass or potassium tianate. Further, fluids may be used which include dielectric fluids or materials such as polysiloxane materials described in U.S. Patent 3,278,673.

WHAT WE CLAIM IS:—

1. A porous polymeric material containing units derived from tetrafluoroethylene, the material having a microstructure characterized by nodes interconnected by fibrils, the material having a matrix tensile strength (as herein defined) of at least 7,300 p.s.i.

2. A porous material in accordance with claim 1, in which the polymer is poly(tetrafluoroethylene), a copolymer of tetrafluoroethylene and ethylene, a copolymer of tetrafluoroethylene and chlorotrifluoroethylene, or a copolymer of tetrafluoroethylene and hexafluoropropylene.

3. A porous material in accordance with either of the preceding claims, in which the fibrils are individual fibrils having diameters of from 5 to 1000 Angstroms.

4. A porous material in accordance with any of the preceding claims, in which the nodes are from 0.5 to 400 microns long.

5. A porous material in accordance with any of the preceding claims, which has not been heated to a temperature above 327°C and has a crystallinity greater than 95%.

6. A porous material in accordance with any of claims 1 to 4, which has been heated to a temperature above 327°C and has a crystallinity below about 95%.

7. A porous material in accordance with claim 6, which has a matrix tensile strength of at least 9290 p.s.i.

8. A porous material in accordance with claim 7, having a thermal conductivity of from 0.17 Btu/hr/sq.ft./°F./in. to 0.85 Btu/hr/sq.ft./°F./in.

9. A porous material in accordance with claim 7, having a dielectric constant of 1.2 to 1.8.

10. A porous material in accordance with claim 7, having a permeability to nitrogen of from about 1×10^{-4} to 1×10^{-1} metric units.

11. A porous material in accordance with claim 1, which has a matrix tensile strength of about 12,800 p.s.i., of about 16,800 p.s.i., of about 20,300 p.s.i., of about 25,200 p.s.i., of about 30,000 p.s.i., of about 36,200 p.s.i., or of about 117,000 p.s.i.

12. A porous material in accordance with any of the preceding claims, which includes a filler.

13. A porous material in accordance with claim 12, in which the filler is asbestos, carbon black, a pigment, mica, silica, titanium dioxide, glass, potassium titanate, or a dielectric fluid.

14. A porous material in accordance with claim 13, in which the filler is a polysiloxane.

15. A porous material in accordance with any of the preceding claims in the form of a film, a tube, a filament, or a rod.

16. A porous material in accordance with any of the preceding claims, in which the polymer has been expanded such that its final length in the direction of expansion is from twice to fifteen times its original length.

17. A porous material in accordance with

claim 16, in which the final length is about three times its original length.

18. A porous material in accordance with claim 16, in which the final length is about five times its original length.

19. A porous material in accordance with claim 16, in which the final length is about seven times its original length.

20. A porous material in accordance with any of the preceding claims, which has been compressed.

21. A porous polymeric m..ial in accordance with claim 1, substantially as herein described.

22. A porous polymeric material according to claim 1, substantially as herein described with reference to any of the examples.

23. A process for the production of a porous polymeric material containing units derived from tetrafluoroethylene, which process comprises forming a shaped article of the polymer by paste-forming extrusion technique, and expanding the shaped article after removal of lubricant therefrom, by stretching the shaped article at an elevated temperature and at a rate exceeding 10% per second of its original length.

24. A process in accordance with claim 23, in which expansion is performed with the shaped article at a temperature of from 35° to less than 327°C.

25. A process in accordance with claim 24, in which expansion is performed with the shaped article at a temperature of from 93° to less than 327°C.

26. A process in accordance with any of claims 23 to 25, in which the rate of expansion is about 30% per second, about 100% per second, about 500% per second, about 1000% per second, about 5000% per second, about 10,000% per second, or about 40,000% per second.

27. A process in accordance with claim 23, in which the shaped article before expansion has an amorphous content of not more than 3.5%.

28. A process in accordance with any of claims 23 to 27, in which the polymer is poly(tetrafluoroethylene), a copolymer of tetrafluoroethylene and ethylene, a copolymer of tetrafluoroethylene and chlorotrifluoroethylene, or a copolymer of tetrafluoroethylene and hexafluoropropylene.

29. A process in accordance with any of claims 23 to 28, in which the expansion is effected in only one direction.

30. A process in accordance with any of claims 23 to 28, in which the expansion is effected biaxially.

31. A process in accordance with any of claims 23 to 30, wherein the resultant porous article is compressed.

32. A process in accordance with any of claims 23 to 31, in which the expansion is effected such that the final length of the article in the direction of expansion is from twice to fifteen times its original length.

33. A process in accordance with claim 32, in which the final length of the article is about three times its original length.

34. A process in accordance with claim 32, in which the final length of the article is about five times its original length.

35. A process in accordance with claim 32, in which the final length of the article is about seven times its original length.

36. A process in accordance with any of claims 23 to 35, in which the expanded article is subsequently heated to a temperature above the crystalline melting temperature of the polymer.

37. A process in accordance with claim 23, substantially as herein described.

38. A process in accordance with claim 23, substantially as herein described with reference to any of the Examples.

39. A porous polymeric material when produced by a process in accordance with any of claims 23 to 38.

40. A coaxial cable insulated with a porous polymeric material in accordance with any of claims 1 to 22 or 39.

41. A coaxial cable in accordance with claim 40, wherein the insulation is in the form of a tape and the polymer is poly(tetrafluoroethylene).

42. A coaxial cable substantially as herein described with reference to Example 12.

43. A composite structure comprising a first substrate of a porous polymeric material in accordance with any of claims 1 to 22 or 39, bonded to a second substrate.

44. A composite structure in accordance with claim 43, in which the second substrate is of a porous polymeric material in accordance with any of claims 1 to 22 or 39.

45. A composite structure in accordance with claim 44, in which the second substrate is bonded to the first substrate by amorphous locking of two abutting poly(tetrafluoroethylene) surfaces.

46. A composite structure in accordance with claim 43, substantially as herein described with reference to Example 9.

47. An article comprising a porous material in accordance with claim 7, having poly(methyl methacrylate) or an epoxy resin within the pores thereof.

48. An article in accordance with claim 47, in the form of a bearing.

49. An article in accordance with claim 47, substantially as herein described with reference to Example 11.

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Fig. 1.

Direction of Uniaxial Expansion

Fig. 2.